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POROUS ALUMINUM OXIDE FILMS OBTAINED BY DOUBLE-SIDED ANODIZATION

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Abstract. Anodic aluminum oxide films are widely used to obtain many types of organic and inorganic nanomaterials and are of practical importance in studying the optical properties of nanomaterials synthesized from them. This work presents a method of two-sided and two-stage anodization for obtaining anodic aluminum oxide films with periodic and regularly spaced pores. The method of anodic oxidation of aluminum in solutions of acidic electrolytes makes it possible to quite easily vary the parameters of the porous structure of Al_2O_3. Oxalic acid was used as an electrolyte for “soft” anodizing of the aluminum plate, and ethyl alcohol and a solution of orthophosphoric acid and chromic anhydride were used to pre-clean and polish the aluminum plate. Anodization was carried out at low temperatures, as a result of which it was possible to obtain an aluminum oxide film with a high degree of ordering of pores, the sizes of which ranged from 60 to 110 nm, and the distance between the pores was in the range of 13–27 nm. Absorption and reflection spectra of a porous film of anodized aluminum were obtained, where good absorption of the films is observed in the short-wavelength region of the spectrum, and the maximum value of the refractive index is observed in the short- and long-wavelength regions of the spectrum.

Keywords: Transparent anodic aluminum oxide films, double-sided anodizing, porous membranes, anodizing at low temperatures, barrier layer.

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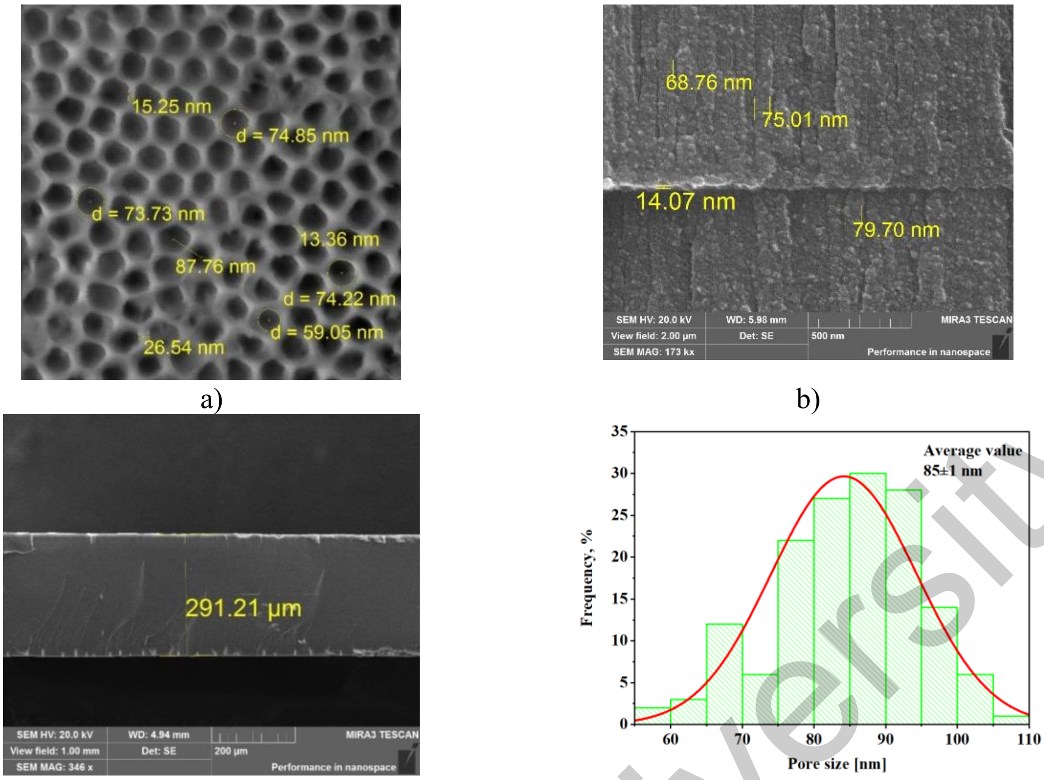
Anodic aluminum oxide (AAO) films with periodic and regularly spaced pores have a wide range of applications. AAO is used to obtain many types of organic and inorganic nanomaterials, which are widely used in optics, energy storage, sensors, molecular sieves for gas separation, surface-enhanced Raman scattering [1], ion current rectification [2], biological antibacterial treatment [3], food industry [4] and many other areas. By changing the experimental conditions and preparation processes, it is possible to obtain AAO films with different porous structures [5]. Transparent AAO films are of practical importance in studying the optical properties of nanomaterials synthesized from them. Transparent AAO films with barrier layers separated from aluminum substrates have nonlinear diode-type current-voltage characteristics and ion rectification properties and are used in biosensing, bioseparation, nanofluidic electronics, etc. [6].

Due to the fact that ordering of the structure occurs during film growth, the upper side of the membrane is characterized by a chaotic arrangement of pores. To obtain films with an ordered structure throughout the entire volume, two-stage anodization of the films was carried out. The method of anodic oxidation of aluminum in solutions of acidic electrolytes makes it possible to quite easily vary the parameters (pore diameter, distance between pores, film thickness) of the Al_2O_3 porous structure. The production of aluminum oxide layers was carried out under conditions of “soft” anodization using a two-sided method. The thickness of the films obtained by this method is directly proportional to the duration of electrochemical oxidation, and the rate of formation of the oxide layer varies from 2 to 5 μm/h. It should be noted that the temperature of the electrolyte is the most important parameter, since at a constant acid concentration it determines the rate of dissolution of the oxide layer at the oxide/electrolyte interface. After preliminary surface preparation, the first anodic oxidation of aluminum was carried out in a solution of 0.3 M $(COOH)_2$. After this, subsequent (second) anodic oxidation was carried out under the same conditions as during the first oxidation. In this case, it is possible to obtain an aluminum oxide film with a high degree of pore ordering.

In Figures 1 (a) and (b) are shown SEM images of one of the surfaces of a transparent alumina film. The pictures show a typical ordered porous structure. The size of the ordered pores varies in the range of 60–110 nm, as shown in Figure 1 (d). The distance between the pores was in the range of 13–27 nm. The SEM image of the transverse cleavage of the transparent AAO film is shown in the same Figure 1 c. The film thickness is about 291 μm. The transverse cleavage is divided into upper and lower layers, separated by a barrier layer whose size is on the order of 14 nm (Figure 1 b).

The absorption spectrum of a porous anodized aluminum film is shown in Figure 2. Anodized aluminum films are practically opaque in the spectral range of 400-700 nm. The observed good absorption of anodized aluminum films $\lambda<400$ nm in the short-wavelength region of the spectrum with the maximum at 380 nm corresponds to an interband transition from the valence band to the bottom of the conduction band. This region corresponds to transitions from final states of the valence band to broadened states of the conduction band in aluminum oxide [7]. In the long-wavelength part of the absorption spectrum of films at $\lambda>450$ nm, a broad band with a maximum at 570 nm is observed, which may be associated with light scattering in porous structures.

The diffuse reflectance coefficient of films is 27% at 430 nm and decreases as the wavelength of light increases (Figure 3a). Such pronounced peaks are observed in thin AAO films, the thickness of which is comparable to the wavelength [8]. The appearance of such a peak in a thick AAO film is apparently associated with the presence of a barrier layer in the center of the oxide structure. In the range of 550-850 nm, the reflection is on average no more than 10%. The optical constants of thin films of anodized aluminum (k – extinction coefficient and n – refractive index) were determined according to the method [9]. As expected, the extinction coefficient given in Figure 3b for the resulting structure generally follows the absorption spectrum corrected for the reflection and refractive index.



a) b) c) d)

Fig.1. (a) SEM image of the surface of an aluminum oxide film; (b) SEM image of a transverse cleavage of a transparent AAO film; (c) size of a transverse cleavage; (d) histogram of pore size distribution.

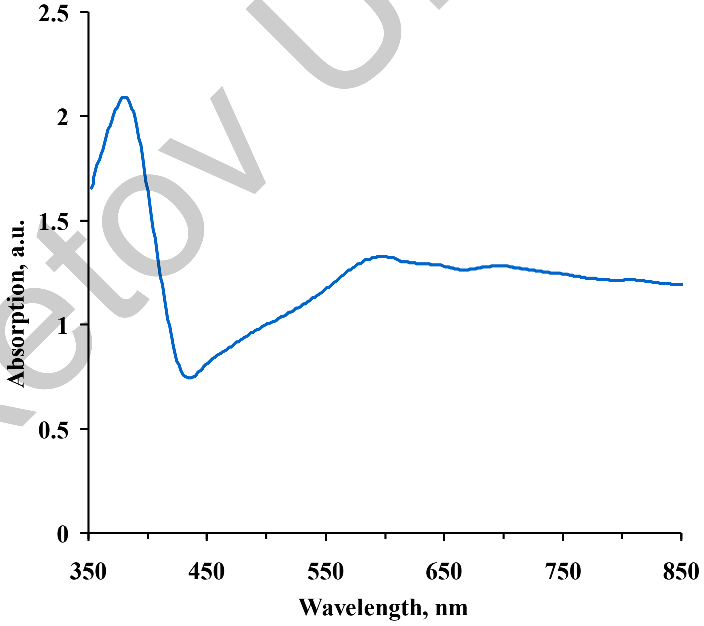


Fig.2. Absorption spectrum of a porous film of anodized aluminum.

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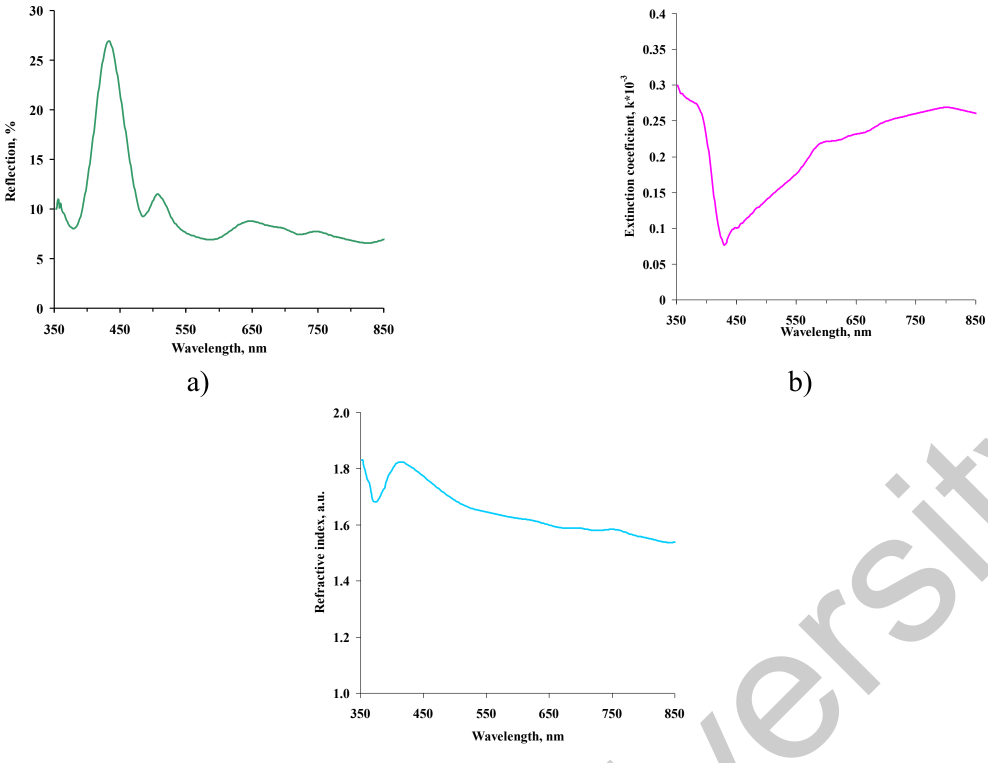

a) b)

c)

Fig.3. (a) Reflection spectrum; (b) dependence of the extinction coefficient on the wavelength; (c) dependence of the refractive index on the wavelength of anodized aluminum films.

The refractive index is one of the fundamental properties of an optical material, since it is closely related to the electronic polarization of ions and the local field within the material. The Figure 3c shows that the maximum value of the refractive index (n=1.82) is observed in the short-wavelength λ=412 nm and gradually decreases in the long-wave part of the spectrum. These results are in good agreement with data obtained by other authors [10].

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